



A review on long-term sorption solar energy storage

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ABSTRACT

In the past decade, long-term sorption and thermochemical heat storage has generated lot of interest. This paper presents the state of the art in this field of research, materials used in these systems and technological difficulties that researchers are set against. An emphasis is put on recent demonstrative projects including absorption and adsorption for long-term solar energy storage. It emerges that considerable breakthrough have been made. Even though there is no mature long-term sorption or thermochemical energy storage yet, primarily due to the high cost of materials, the suitability of this technology to long-term storage remains its main power of attracting.

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1. Introduction

With the diminishing reserves of fossil fuels, the increasing energy demand and the greenhouse gas emissions rise, buildings energy consumption is at a critical stake, as 40% of energy demand in Europe is used in buildings [1]. Developing more energy efficient and environmentally friendly devices is essential to reach the “3E”

objectives, conciliating clean Environment, sustainable Energy policy, solid Economy and social development.

The main role of energy storage systems is to reduce the time or rate mismatch between energy supply and energy demand [2] (Fig. 1). Solar energy seems to be the most promising renewable energy source [3–5] but a lot of technical and economic problems have to be solved before large-scale utilization of solar energy can occur. Thermal energy storage remains among the ranks of these problems, especially when talking about long-term storage.

Besides, developing efficient and inexpensive energy storage devices is a necessity [2] when it is admitted that in the coming years, energy supply will be more unstable than in present (Fig. 1):

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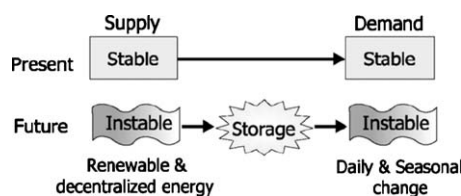


Fig. 1. Trend shift of energy chain between energy supply and demand sides [6].

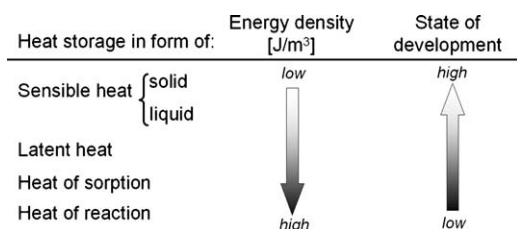


Fig. 2. Energy density of physical and chemical changes.

energy will mostly be accessed by renewable energy sources which are mainly characterized by discontinuity of production periods and shift between energy supply and its use [6]. In addition, greater demand fluctuations will appear because of the decentralization of energy production linked to the use of renewable energies [6,7].

Long-term energy storage refers to applications aiming to store energy for a few months or even a whole season (3–6 months) [8,9]. Storage density, defined as the amount of energy accumulated per unit volume or mass [7,10], is in general given in relation to materials but it is also often given in relation to all the tanks and heat exchangers. It depends strongly on the operation temperature range [11]. Mass is an important parameter for applications in term of materials cost. The volume can be important when the system has to be placed in a restricted or costly place such as urban areas [7]. It also has an incidence on the means and costs of containing and maintaining vacuum conditions when necessary.

Heat storage in the form of sensible and latent heat is the most studied technologies and is at an advanced state of development

(Fig. 2) [2,6,12]. In sensible heat storage, thermal energy is stored by raising the temperature of a material [13] and the storage density is equal to the product of the specific heat of this material by the temperature change [9]. Hot water storage (hydro-accumulation), underground thermal energy storage (aquifer, borehole, cavern, ducts in soil, pit), rock filled storage (rock, pebble, gravel) are the main applications of sensible heat storage, and are described in Ref. [14].

Latent heat is the quantity of heat absorbed or released by a material, while changing its phase at a constant temperature. A phase change material (PCM) melts and takes up energy corresponding to the latent heat of the material when the temperature increases above the melting point [14]. Conversely, the latent heat is released when the material is cooled back and the PCM solidifies. Over 150 PCMs and their properties were listed by Zalba et al. [15]. Studies using various types of PCMs show that latent heat storage using PCMs can store 5–14 times more heat than sensible heat materials [13], which are regardless relatively cheaper [9]. However, as physical thermal storage systems (sensible heat or phase change) progressively lose thermal energy [6], they are not suitable for long-term storage [16].

The relevance of storage systems based on sorption phenomena thus lies in their high energy density and their negligible heat loss and the repetitiveness of storage operations [6,17–19]. Materials used in sorption storage have the highest storage density of all repetitive storage media [9] and some of the materials may even offer storage density close to that of biomass [20] (Fig. 3, [21]). With the aforementioned characteristics of sorption materials, it is possible to consider long-term solar energy storage, in particular seasonal storage, based on sorption, a process that gained recently a renewal of interest in research platforms.

This paper presents the state of the art on Sorption long-term Solar Heat Storage (SSHS) and barriers that researchers have to overcome. An emphasis is put on recent projects including absorption and adsorption.

2. Terminology

The use of the expressions “chemical storage”, “thermochemical storage” and “sorption storage” differs from an author to another

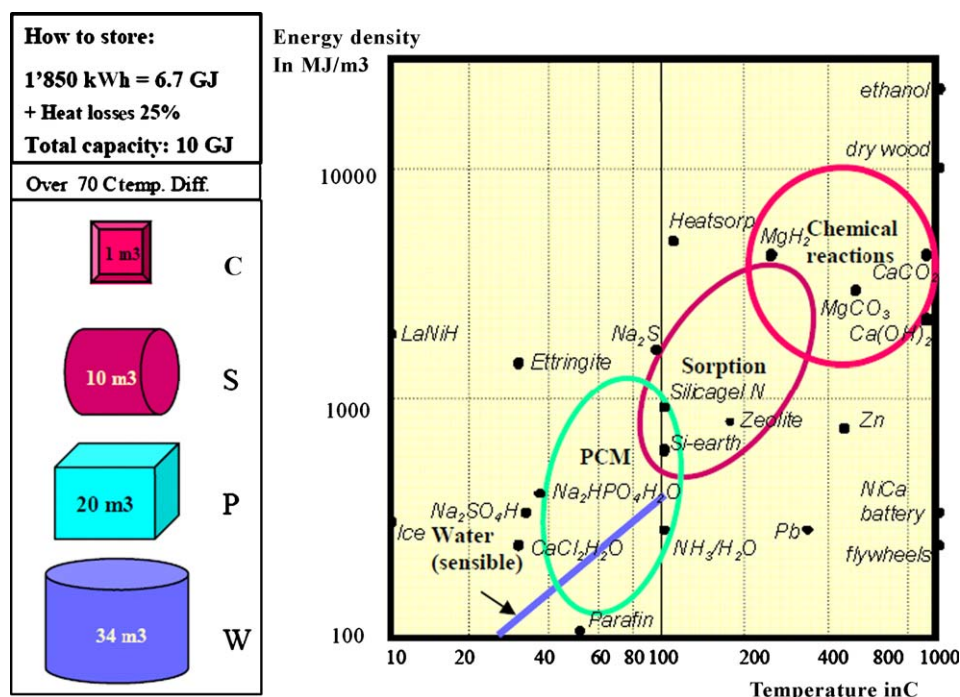


Fig. 3. Energy density of high energy storage methods (adapted from [21,8]).

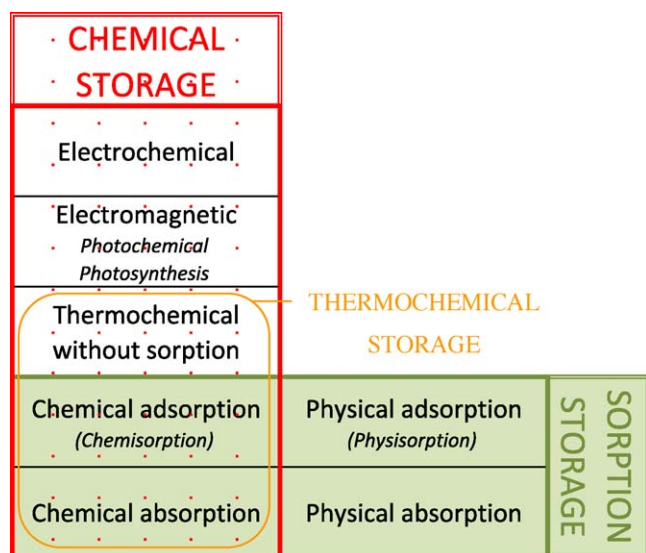


Fig. 4. Chemical storage and sorption storage classification.

[9,20,22–27] and it is difficult to find clear boundaries between these expressions. Chemical energy storages use reversible chemical reactions to store energy in chemical bounds [2]. As shown in Fig. 4, this energy is stored by supplying energy as thermal energy (thermochemical reactions), electrical energy (electrochemical reactions such as in batteries), or as electromagnetic radiation (photochemical reactions and photosynthesis) [2,28–30].

Sorption can be defined as a phenomenon of fixation or capture of a gas or a vapour (sorbate) by a substance in condensed state (solid or liquid) called sorbent [17,31]. Sorption phenomena can involve both thermo-physical and thermo-chemical aspects [32,33]. The term “sorption” is a general term which includes both absorption and adsorption [31,34] (Fig. 4). Adsorption is defined as a phenomenon in which a liquid or a gas enters a solid or a liquid [31,35,36] but, considering storage applications, this term is usually relative to the absorption of a gas by a liquid (absorbent). In the same way, adsorption is usually used to designate a phenomenon of binding of a gas on a surface of a solid or porous material [17,33,35] when a more general acceptance of the word refers to a surface phenomenon: an attachment of gas or liquid phase of a component to the surface of another substance [31,37]. Adsorption is split into two types: physical adsorption (physisorption) and chemical adsorption (chemisorption or solid/gas chemical reaction) [31–34,37,38]. The former is due to Van der Waals forces, the latter involves valency forces. Chemisorption processes offer larger heat of sorption than physisorption [37,39] but may be irreversible [33]. A good comparison of both phenomena has been given in Refs. [33,34,38].

The thermodynamic variance can also be used to distinguish sorption phenomena: variance equals to two for physical adsorption and absorption whereas it equals to one for chemisorption [38,40]. Indeed, systems involving chemisorption require only one state variable to be specified (e.g. pressure or temperature) when two state variables (temperature, pressure or degree of sorbate loading) are needed to describe completely a physical adsorption/absorption equilibrium [40,41].

Sorption and thermochemical storage systems use a reversible physico-chemical phenomena to store energy [17,42]:



A/B is called a working pair or sorption couple. Under the influence of a heat supply, a compound AB is dissociated into components A and B which can be stored separately (endothermic

phenomenon). When A and B are put in touch, component AB is formed with a heat release (exothermic phenomenon) [9]. Energy can therefore be stored with negligible thermal loss [6,9] since heat is not kept in sensible or latent form but as a chemical potential.

Sorption is also used in heat pump technologies [19,41], solar refrigeration [38,43], long distance energy transportations [44,45], waste heat promotion [6] or as a buffer between heating net and space heating systems [46].

Sorption processes dedicated to storage can be classified as open or closed system [18]. Illustrations on common configurations will be given in Section 4.2. In open systems, which operate at atmospheric pressure, the working fluid vapour is released to the environment, which means that only water is used for those systems. By contrast, materials isolated from the neighbourhood and fluid(s) circulating in closed circuits characterize closed systems. Closed systems are able to supply higher output temperatures for heating applications than open systems [11]. However, the regeneration of closed systems usually requires a higher level of temperature than open systems; this results in lower solar collector efficiency when considering solar heat storage [47]. In closed systems that operate in vacuum conditions, the presence of non-condensable gases can reduce strongly the system performance [26,48].

The closed SSHS process is similar to that of chemical heat pumps with a major difference. A chemical heat pump works usually with two simultaneous circulations (continuous process) and needs therefore a condenser and an evaporator as well as a desorber and an ab/adsorber. Heat storage systems work in batch mode so that vessels are needed to store the products. In addition, the desorber might be used as an ab/adsorber and the condenser also as an evaporator [48]. The SSHS operates in charging (regeneration) during sunny periods and discharging during energy demand periods. Solar energy is captured by solar thermal collectors (during summer or days of sunshine in mid season), which provide heat to the component AB in Eq. (1): it is the regeneration or desorption or charging phase. A and B are stored separately in different tanks. In winter, bringing together A and B turns the chemical potential into heat: it is the ab/adsorption or the discharging phase.

The following sections are focused on sorption storage, which involves a part of thermochemical storage in accordance with Fig. 4.

3. Main challenges and selection criteria

In SSHS, researchers are mainly submitted to the following challenges [49]:

- the choice of the best system (closed or open);
- the storage density optimisation linked to the choice of materials (this point will be detailed in the following);
- the vessels/tanks design;
- the heat exchangers design and the reactors configuration (these points will be detailed below);
- pressure drop;
- the low-temperature heat source in winter;
- efficiency;
- cost.

Materials appear to play a key role in these challenges [9]. A suitable material can store the energy without heat loss and is able to release this energy immediately when it is needed [50]. There are a great number of materials that could be used for sorption when focusing only on the thermodynamic principle of reversible reactions [17]. Some technical, economic or ecological criteria lead

to a closer set. Indeed, usual selection criteria of materials used in sorption machines are [18,40,41,51,52]:

- high affinity for the sorbent by the sorbate: this has an effect on the rate of the ab/adsorption reaction, which is important for an usable power density;
- better volatility of the sorbate (than the sorbent) in absorption;
- high storage density;
- high thermal conductivity (in particular for adsorption) and high heat transfer from sorbate to heat exchangers;
- regeneration (charging) temperature as low as possible: this results in higher solar collector efficiency;
- heat source needed for the evaporation during discharging period at relatively low temperature;
- environment safety, non-toxicity, low Global Warming Potential and Ozone Depletion Potential;
- non-corrosiveness of materials;
- good thermal and chemical stability under operating conditions (temperature, pressure);
- moderate operating pressure range: no excessive pressure conditions and especially no high vacuum;
- low material cost;
- etc.

Another key challenge is linked to reactors, Zondag et al. [53] suggested that separate reactors (Fig. 5) are more suitable than integrated reactors, for seasonal storage. Indeed, integrated reactors are usually used for solid sorption material because the transport of the solid material is not necessary when using such reactors. However, for large storage, which is often the case in long-term storage, all the storage material has to be heated up from the ambient temperature at the beginning of the sorption and has heat loss to the ambient during and after the discharging [53,54]. This results in larger sensible loss especially when the reactor is not divided into compartments. By contrast, in a separate reactor, only little amounts of sorbent and sorbate are to be heated up in the reactor, according to the desired power so that the system is more efficient. The heat exchanger surface is also smaller than in the case of integrated reactor. Moreover, the reactor can easily be insulated since it is smaller. For SSHS purposes, three design cases of separate reactors have been presented and discussed in Ref. [53]: fluidised bed reactor, extruder reactor system, bulk flow reactor system.

Concerning the heat exchangers design, the use of efficient heat exchangers has a non-negligible effect on the global process. Indeed, as aforementioned, the energy storage density is, among others, strongly dependent on the required discharging tempera-

ture. The minimum temperature of discharging is given by the minimum temperature required for the space heating (or domestic hot water production) and the driving temperature differences of heat exchangers ranging from the space heating loop to the heat exchanger of the reactor. Now, the achievable storage density decreases drastically, when higher temperature lift is needed during discharging [11]. So heat exchangers, especially in the reactor, had better a good efficiency. This is all more important since some storage materials have low heat conductivity or low reaction rate. Similar considerations can be applied to the low heat source loop that supplies evaporation energy in winter: the storage density decreases with the temperature of the produced vapour.

4. State of the art

4.1. Materials currently used or studied

Different working pairs or materials, according to their ability to fulfil aforementioned requirements, have been considered in SSHS. Studies aimed to describe physicochemical and thermodynamic properties of materials suitable for long-term storage of thermal energy, since knowledge on materials is a prerequisite to the design of different components of storage units, exchangers and solar plants [18].

In 2004, a study of several (about ninety) potential materials for seasonal storage of solar heat has been carried out by ECN (Energy research Centre of the Netherlands) [52,55], which, after theoretical simulations and comparison according to a “realisation potential” identified the best suitable materials from the first selection (see Table 1). They concluded that magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and iron hydroxide ($\text{Fe}(\text{OH})_2$), appear (theoretically) to be the most promising materials for development of an autonomous thermochemical storage system. Their energy density is one order of magnitude larger than that of hot water storage. Another conclusion of this study is that the cycle storage density is enhanced when using open cycle [55]. However, an advanced study of characterization of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ [56] shows that this material cannot release all the stored heat under practical conditions.

SPF (the institute for Solartechnik Prüfung Forschung) [23] in Switzerland, has investigated zeolite and silicagel in the perspective of seasonal storage in closed adsorption cycle. They concluded that the adsorption process does not offer a potential for long-term storage and is more suitable for cooling applications in a thermally driven heat pump. They estimated also that a sorption involving liquid (absorption) could be more suitable for storage applications

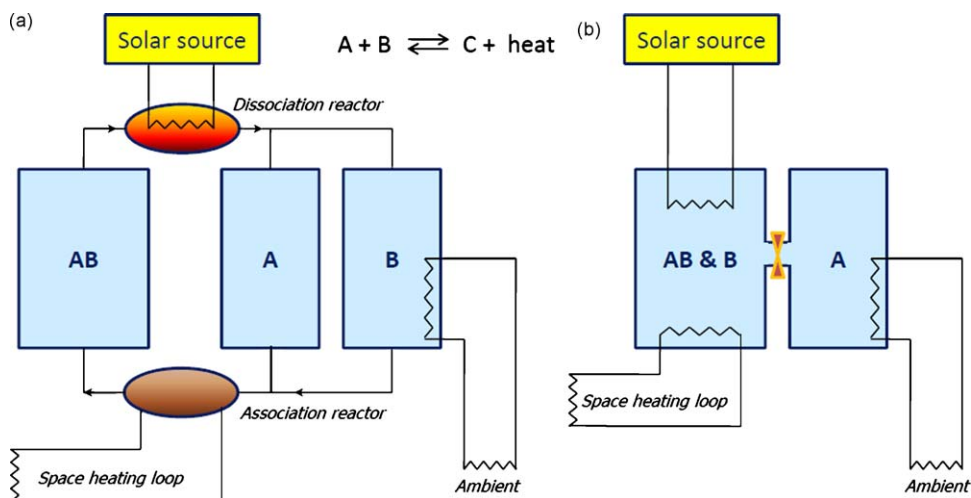


Fig. 5. (a) Separate reactor and (b) Integrated reactor (adapted from [53]).

Table 1

Thermodynamics characteristics and realisation potentials of the top 5 minerals in the study of ECN [52].

Material name	Dissociation reaction			Energy storage density of AB GJ/m ³	Turnover temperature °C	Realisation potential %
	AB \leftrightarrow	B +	A			
Magnesium sulphate	MgSO ₄ ·7H ₂ O	MgSO ₄	H ₂ O	2.8	122	9.5
Silicon oxide	SiO ₂	Si	O ₂	37.9	4065 + HF: 150	9.0
Iron carbonate	FeCO ₃	FeO	CO ₂	2.6	180	6.3
Iron hydroxide	Fe(OH) ₂	FeO	H ₂ O	2.2	150	4.8
Calcium sulphate	CaSO ₄ ·2H ₂ O	CaSO ₄	H ₂ O	1.4	89	4.3

Silicon oxide dissociates at approximately 150 °C with HF (hydrofluoric acid).

than solid adsorption because the liquid can easily be pumped from a tank to another through a reactor. Investigations on the geometrical system structure limitations in a closed adsorption storage system [50] lead them to suggest that a closed solid-gas/liquid sorption system is more suitable for a heat pump or a cooling application than for thermal storage.

A recent generation of storage materials, called Selective Water Sorbents (SWSs) and presenting intermediate behaviours between solid adsorbents, salts hydrate and liquid absorbents with on top of that a better COP than usual adsorbents (silicagel/H₂O, zeolite/H₂O) is under study [57]. A SWS is a two-component material based on a porous host matrix with an inorganic salt inside its pores [58] for example aluminophosphates [59], SAPO-34 or different ion exchanged zeolites [60]. The important advantage of such a composite is the possibility to controllably modify its water sorption properties in a wide range by changing some variables [57].

The couples that have been the basis of specific study in SSHS are:

4.1.1. For absorption

NaOH/H₂O: Refer to the project of EMPA (Swiss Federal Laboratories for Materials Testing and Research in Switzerland) in Section 4.2. Caustic soda is highly corrosive [48]. Special care must be taken when working with this chemical.

LiCl/H₂O: Based on the results presented by ClimateWell (in Sweden) [23,61], this pair is not suitable for seasonal storage, not because of its storage density (253 kWh/m³ LiCl salt), which is 2.7 times higher than that of water (25/85 °C), but because of the high cost of the salt (≈ 3600 €/m³).

LiBr/H₂O: Static simulations made by the LOCIE (Laboratoire Optimisation de la Conception et Ingénierie de l'Environnement, France), based on an evaporation temperature of 5–10 °C to produce heat at 25–33 °C in winter, show storage density between 180 and 310 kWh/m³ diluted solution [62].

4.1.2. For physisorption

Zeolites/H₂O: Zeolites are alumina silicates with high micro-porosity [14] and are considered to be compatible with the most stringent environmental regulations [63]. Apart from natural zeolites (minerals), different types of synthetic zeolites have been developed for special purposes [37]. Alefeld et al. [64], reported by Kato [6], ruled out the use of zeolites in seasonal storage for economical reasons and suggested that zeolites could be used in the load levelling within a district heating net. This idea has been proved by Hauer [46], who, using the synthetic Zeolite 13X, reached experimental storage density of 124 kWh/m³ for heating and 100 kWh/m³ for cooling with COP of 0.9 and 0.86. As synthetic zeolites are expensive, a contrast study of natural zeolites to the synthetic zeolite 13X was made by Baoqi et al. [65]. They reported that natural zeolites could be used as storing material instead of the 13X synthetic zeolite when the heating temperature is below 100 °C.

Silicagel/H₂O: According to Faninger [9], the storage density of silicagel is up to about 4-times that of water (25/85 °C). Silicagel has been used for SSHS (closed cycle) by AEE-INTEC (Institute for Sustainable Technologies, Austria) [54,66] in a series of studies. They achieved experimentally about 50 kWh/m³ of material storage density whereas they had theoretically estimated to reach a storage density of 200–300 kWh/m³ before [67]. Their conclusions reject the idea of using silicagel in long-term storage applications since this material is less efficient than water [66], even for short-term storage applications [54]. See Section 4.2 for more details.

4.1.3. For chemisorption

Na₂S/H₂O: Sodium sulphide presents a high sorption capacity and a high heat of sorption (300 kJ/mole of Na₂S salt = 1.1 kWh/kg) so that it provides a high thermal power density combined with a high energy storage density. In effect, it is a hydrate of Na₂S for example its nonahydrate (Na₂S·9H₂O) [25] or its pentahydrate (Na₂S·5H₂O) [26] that is involved. However, sodium sulphide is very corrosive and operates under high vacuum. This material storage density as measured by Boer et al. [26] on the SWEAT prototype (see Section 4.2) is almost 1.1 kWh/kg (1980 kWh/m³) for heat and 0.7 kWh/kg (1300 kWh/m³) for cooling with COP of 0.84 and 0.57, respectively. Considering the Na₂S·5H₂O, which they used, the material storage density is almost 780 kWh/m³ for heating and 510 kWh/m³ for cooling.

MgSO₄·7H₂O: The magnesium sulphate heptahydrate is shown by Visscher and Veldhuis [55] as presenting theoretically a very good potential in terms of solar energy storage with high density of almost 780 kWh/m³ [66] at temperature level of 122 °C. MgSO₄·7H₂O is non-toxic and non-corrosive but expensive (Table 2). However, some experiments performed by EDF R&D (Energie De France, France) [68] show that the practical use of pure magnesium sulphate is quite difficult because of its low power density. van Essen et al. [56] have observed the same phenomenon in a study of characterization of this material. They concluded that the application of magnesium sulfate as thermochemical storage material is quite problematic.

4.2. Projects based on long-term sorption storage

Over the past 10 years, some international programmes aiming to show the feasibility and the relevance of long-term energy storage (solar energy in particular) by sorption have seen the light of day:

- HYDES (high energy density sorption heat storage for solar space heating) from 1998 to 2001 [69–71].
- MODESTORE (modular high energy density heat storage) from 2003 to 2006 [10,70,71].
- “Task 32: advanced storage concepts for solar and low energy buildings” from 2003 to 2007 [49,66]. Table 2 summarizes the main characteristics of systems studied during this Task.

Table 2
Main achievements in “Task 32: advanced storage concepts for solar and low energy buildings” [66].

Parameter	TCA, 80–100 °C	NaOH, 95 °C test, 150 °C calculated	Modestore, 88 °C	SPF, 180 °C	Monosorp, 180 °C	ECN, 150 °C
Type of technology	Closed three phase absorption	Closed two phase absorption	Closed adsorption	Closed adsorption	Open adsorption	Closed thermo-chemical
Cost of material	3600 €/m ³	250 €/m ³	4300 €/m ³	2–3000 €/m ³	^a 2500–3500 €/m ³	4870 €/m ³
Storage materials weight	LiCl salt 54 kg Water 117 kg Steel 47 kg	NaOH 160 kg Water 160 kg	Silica gel 200 kg Water 30 kg Steel 100 kg Copper 50 kg	Zeolite 13X 7 kg	Zeolite 4A 70 kg Steel 10 kg	MgSO ₄ ·7H ₂ O
Storage capacity for heat	35 kWh	8.9 kWh	13 kWh	1 kWh	12 kWh	–
Floor space required for prototype	0.46 m ²	2 m ²	0.4 m ²	0.09 m ²	0.4 m ²	–
Energy density of material (NRJ4.1) (ratio to water 25/85 °C)	253 kWh/m ³ (3.6)	250 kWh/m ³ (3.6)	50 kWh/m ³ (0.71)	180 kWh/m ³ (~3)	160 kWh/m ³ (2.3)	420 kWh/m ³ (6.1)
Energy density of prototype (NRJ4.1) (ratio to water 25/85 °C)	85 kWh/m ³ (1.2)	5 kWh/m ³ (0.07)	33.3 kWh/m ³ (0.48)	57.8 kWh/m ³ (~1)	120 kWh/m ³ (1.7)	–
Energy density of prototype – cold (ratio to water 7/17 °C)	54 kWh/m ³ (4.7)	–	–	–	–	–
Charge rate	15 kW	1 kW	1.0–1.5 kW	–	2.0–2.5 kW	–
Discharge rate	8 kW	1 kW	0.5–1.0 kW	0.8/1.8 kW	1.0–1.5 kW	–
Estimated size for 70 kWh (ratio to water 25/85 °C)	0.64 m ³ (1.6)	1.3 m ³ (0.75)	1.7 m ³ (0.59)	1.2 m ³ (~1)	0.54 m ³ (1.9)	^b 0.4 m ³ (2.5)
Estimated size for 1000 kWh (ratio to water 25/85 °C)	5.3 m ³ (2.7)	5 m ³ (2.9)	23 m ³ (0.62)	17 m ³ (~1)	7.7 m ³ (1.9)	^b 5.6 m ³ (2.5)

^a Cost for large quantity of extruded material is unknown and is estimated for zeolite 4A.

^b Estimations are based on experimental storage density of ~420 kWh/m³ for reaction MgSO₄·6H₂O + heat → MgSO₄·0.2H₂O + 5.8H₂O.

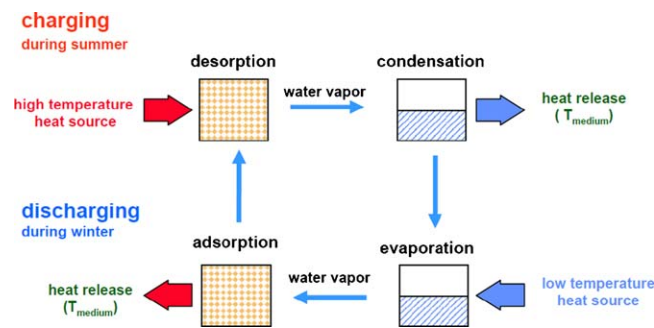


Fig. 6. Operation principle of closed adsorption system [75].

- A new task, “Task 42”, has just been initiated by the IEA for 3 years (2009–2012). The overall objective of this new task is to develop advanced materials and systems for the compact storage of thermal energy [72,73].

The following section describes some projects of the aforementioned programmes and other recent projects as far as long-term sorption storage is concerned.

4.2.1. SSHS by physisorption

AEE INTEC Modestore (modular high energy density heat storage) [54]: In the framework of the HYDES project [10], AEE INTEC in Austria, has built a first prototype in order to observe the performance of a sorption system combined to solar collectors of 20.4 m² for heating and domestic hot water production [70]. It was a closed adsorption system using silicagel/H₂O as shown in Fig. 6. To charge the system, the silicagel is heated throw a heat exchanger with energy from solar collectors at about 88 °C: water vapour is released (desorption) and condensed in a condenser by an external cooler. The vapour condensed and the dry adsorbent are then stored separately with only sensible heat loss. In discharging period, the stored water is evaporated in an evaporator connected to a silicagel store that adsorbs the vapour and releases the useful heat. The experimental results achieved are 20% less than theoretical predictions from simulations (storage density: 150 kWh/m³ of silicagel).

MODESTORE [54] was the occasion of development of a “second generation” prototype and the integration of essential components (reactor, heat exchangers) into a block unit [10]. But the performance achieved with this unit failed to meet expectations: the material storage density dropped to only 50 kWh/m³, that is 30% less efficient than water storage [66]. Indeed, experiments showed that the temperature lift is not sufficient over water content of the silicagel of about 13%. In addition, temperature levels of flat-plate solar collectors and available heat sinks can not allow desorption under water content of 3%: the material has to operate in a water content range of 3–13%. The study has concluded to the unsuitability of the combination silicagel/H₂O for seasonal storage [74] and has suggested for further projects other materials combination such as SWS-1L, Mitsubishi FAM-Z02 and some zeolites [54,66]. However, a storage plant is actually in experimentation for a field test with silicagel/H₂O [54]. The main industrial partner of the project is currently commercialising this technology as heat pumps without storage.

ITW Monosorp [8,23,74,75]: The German project named Monosorp, conducted at ITW (Institute of Thermodynamics and Thermal Engineering) in the University of Stuttgart (Germany), has the potential to permit a heat seasonal storage with 8 m³ of zeolite 4A for a single-family passive house. This concept of open adsorption (Fig. 7), which has been proved and tested in a laboratory, begun in 2006.

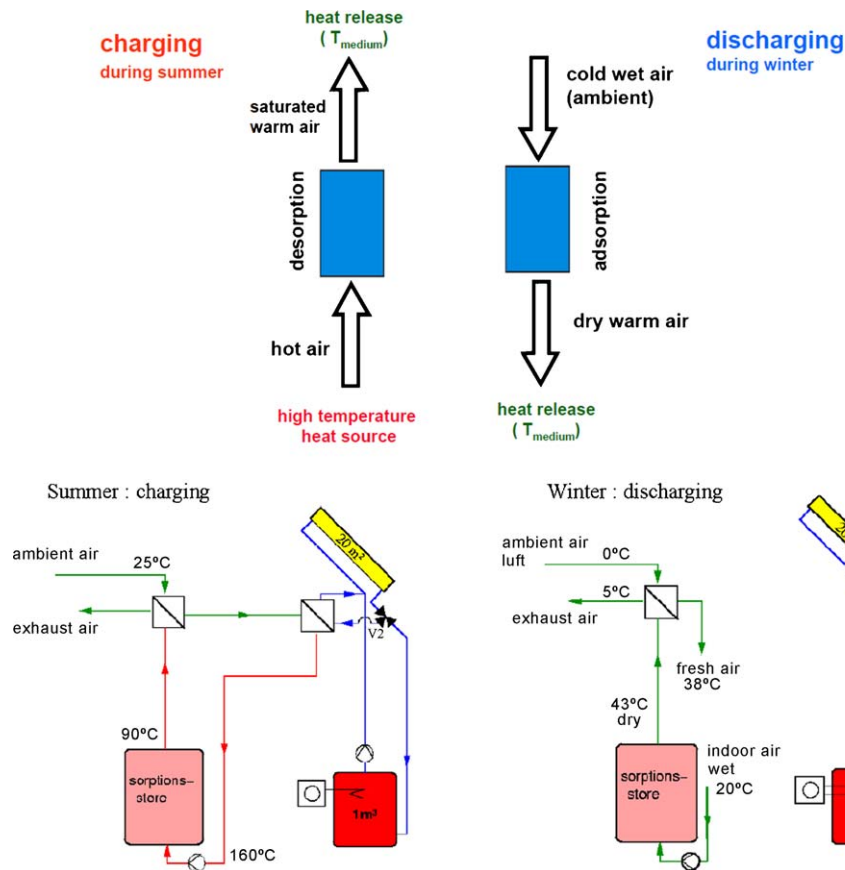


Fig. 7. Operation principle of open adsorption system [75].

During the regeneration phase, in particular in summer, solar excess heat is used to heat the incoming ambient air in a heat exchanger. This air flows through the storage and dries the zeolite. The exhaust air is used to pre-heat the inlet air. During discharging periods, especially in winter, wet indoor air is blown through the sorption storage: the zeolite absorbs the humidity and releases heat that is transferred to the incoming cold air in the ventilation heat exchanger. This warm air is then used for the heating of the building.

The system, which is very simple and flexible, compared to other sorption processes, was sized for weekly cycles so that it could be tested under varying conditions. It is designed with a honeycomb structure in order to improve adsorption kinetics and to reduce pressure losses along the process length. Experimental

conditions have been realised to demonstrate the technical feasibility of the project in field conditions (see Table 2). However, the desorption temperature is very high, around 180 °C, which makes the use of solar heat difficult with this concept.

Sorption energy storage on district heating net in Munich [46]: The system, studied by ZAE Bayern (Center for Applied Energy Research) in Germany, is not specifically a long-term storage solar energy application. It is an open adsorption system used as a buffer in a district heating network to store 1300 kWh for the heating during 14 h of a school building with a maximum power of 135 kW (Fig. 8). This system, which stores without loss as long as wanted, is charged in periods when energy is available from the net in off-peak hours and can therefore be independent from the net at peak demand periods [70]. The system, developed in 1997/1998,

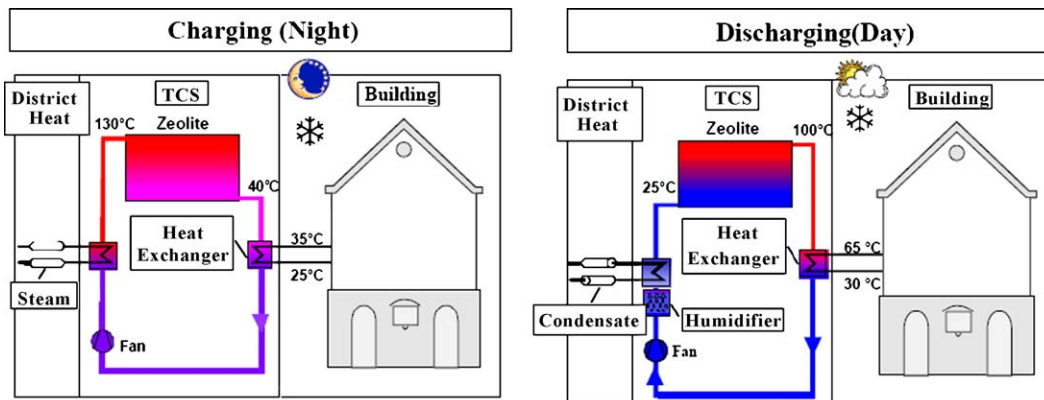


Fig. 8. Open adsorption energy storage system on district heating net in Munich [46].

uses zeolite 13X as adsorbent and is connected to a district heating net in Munich. The storage density is 124 kWh/m^3 for heating and 100 kWh/m^3 for cooling with COP of 0.9 and 0.86, respectively.

4.2.2. SSHS by chemisorption

MCES (Modular Chemical Energy Storage) [25]: The prototype was built and experimented at laboratory scale at Chiang Mai University (Thailand). The project aimed to improve the performance of a sodium sulphide/water chemical energy storage previously designed [76]. In this project, the aim is to store both heat and cold. In the regeneration phase (Fig. 9), high temperature heat is supplied to the reactor located at the top of MCES: water vapour is desorbed and condensed by cooling water in a condenser. The condensed water flows down to the evaporator where it is stored. During the discharging phase, heat is extracted from the refrigerated space into the evaporator, in which a cooling effect is produced. The evaporated water flows up by buoyancy force into the reactor, where it is adsorbed by the sodium sulphide: useful heat is released to the circulated cooling oil.

The main interests of this concept are the modular design (the reactor, the evaporator and the condenser aligned into the same and straight line), the integrated oil bath that results in a low temperature source required (about 79.5°C) and the use of graphite additives. Graphite additives (30% by the mass) are mixed with the sodium sulfide nanohydrated salt ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) similarly to the techniques stated in Wongsuwan et al. [77] in order to improve thermal conductivity and increase the reaction area. It reaches a COP of 1.11 (heating + cooling).

SWEAT (Salt-Water Energy Accumulation and Transformation) [26]: SWEAT project, conducted by Boer et al. [26] at ECN, is centred on the development of a prototype of modular energy storage system for cooling in buildings and industrial applications. This closed solid-sorption system uses sodium sulphide and water ($\text{Na}_2\text{S}/\text{H}_2\text{O}$) with a regeneration temperature limited to 83°C . The achievements observed during the test of the prototype are

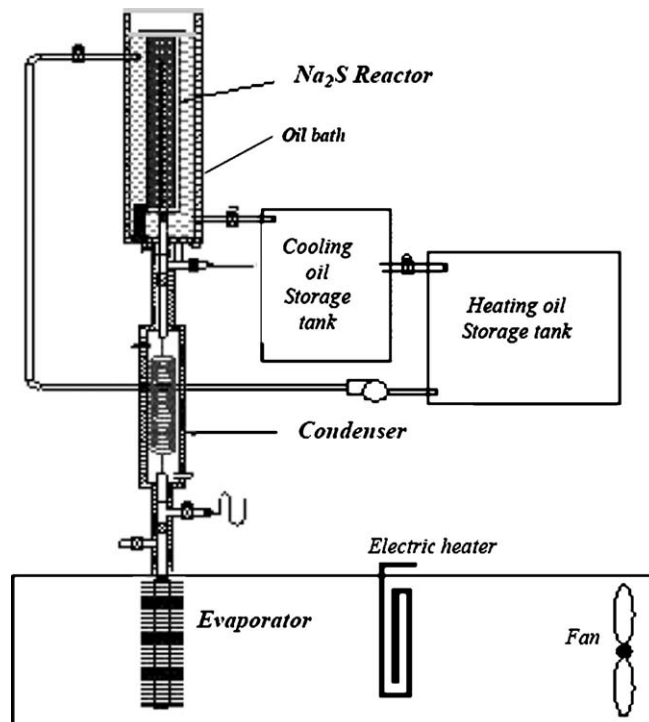


Fig. 9. The schematic diagram of the Modular Chemical Energy Storage (MCES) [25].

compatible with the theoretical values predicted from simulations: a heat storage density of almost 1.1 kWh/kg and a cold storage of almost 0.7 kWh/kg . These values correspond to materials density of almost 780 kWh/m^3 for heating and 510 kWh/m^3 for cooling. Some solutions have been used to minimize corrosion: use of stainless steel for vessels and copper

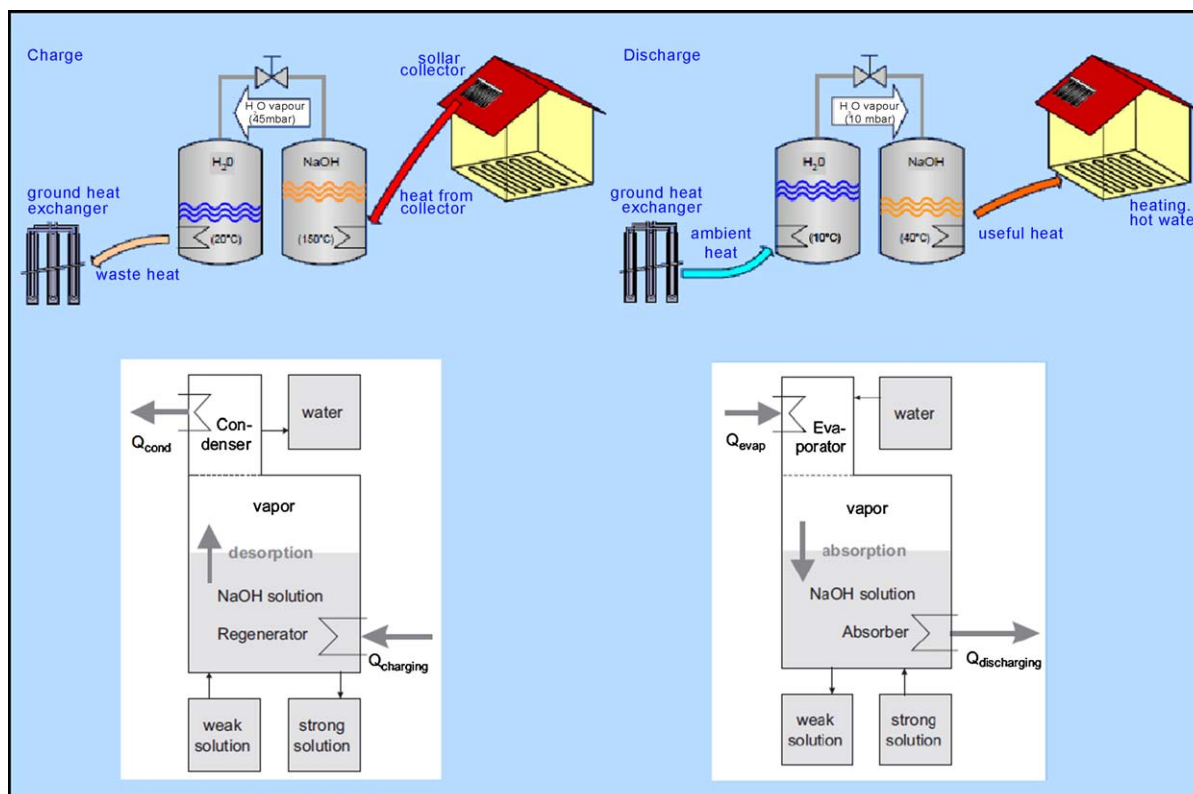


Fig. 10. Operation principle of closed absorption storage [48].

wire-fin coated by standard epoxy powder for the sorbent heat exchanger. The next step of the project would be the monitoring of installations in field tests.

Thermochemical storage using composite materials [68]: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has been investigated by the EDF R&D. The reactor is an open system and the water vapour is taken from the ambient air. Despite the high theoretical energy density of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (dense salt: 780 kWh/m^3), the rate of the reaction and the power delivered is not sufficient for practical use. Therefore, the material needs to be dispersed over a larger exchange surface to react at suitable rate and to release greater thermal power. Obviously, this decreases the storage density. One of the objectives of the project was to optimise the heat transfer or the power density of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by using various porous matrixes to disperse this salt while preserving the energy density as high as possible. Composite materials made of magnesium sulphate and sorption materials, such as zeolites and silica gels, were prepared in such a way that the porosity of the sorption materials is preserved. The water vapour can therefore react with both the salt and the matrix. These composite materials are designed with 50% of the theoretical energy density of the dense salt.

The results show that zeolite/ MgSO_4 composite is more satisfactory than the others. Indeed, temperature lifts around 30°C and maximal power of 28 mW/g have been obtained during the hydration of the zeolite/ MgSO_4 composite; lower values were obtained with pure zeolite, silica, or silica/ MgSO_4 composite tested under the same conditions. EDF R&D is currently investigating other composite materials made of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in order to achieve an energy density of $150\text{--}400 \text{ kWh/m}^3$ at a storage temperature compatible with solar thermal panels.

4.2.3. SSHS by absorption

EMPA NaOH/ H_2O [48]: This project, which had firstly been abandoned for financial reasons [78,79], has obtained a funding [8] in 2006 for the study of a prototype of long-term solar heat storage based on the absorption of water by sodium hydroxide (caustic soda, NaOH) in a closed system.

As shown in Fig. 10, during charging phase, solar heat is supplied to the low-concentration solution in the regenerator. The water vapour is desorbed, flows to the condenser where it condenses. The condensed water is collected inside the water storage tank. To discharge the NaOH storage, the stored water is evaporated in an evaporator using a low temperature source. The vapour is absorbed by the highly concentrated NaOH lye in the absorber and heat is released. The main advantage of NaOH is its cost in relation with its storage density [23] (Table 2).

A calculation made for a single family home according to the passive house standard (120 m^2 , heat demand at $35^\circ\text{C} = 15 \text{ kWh/m}^2$, Domestic Hot Water $\approx 50 \text{ l/day}$ at 60°C , evaporator temperature $= 5^\circ\text{C}$) results in a total storage volume of 7 m^3 , including tanks and heat exchangers, in a two stages process. The experimental measures performed on the prototype during charging have met the expectations of EMPA. The maximum attainable absorber temperature was 95°C and the lowest condenser temperature reached was 13°C , corresponding to a lye concentration of 62 wt%. This concentration value is approximately 7 wt% higher than expected.

To improve the heat production temperature level during discharging process or to reduce the required temperature level during charging process, a double-stage system can be imagined as illustrated in Fig. 11. The overall working principle is similar to the common system (single-stage process) except for an added regenerator 2, condenser 2 and heat exchanger. To regenerate the storage, the NaOH solution flows from regenerator 1 and is split up into two flows: the first part enters condenser 2 and the second part enters regenerator 2. The condenser 2 is working as an absorber, which absorbs the vapour desorbed in regenerator 2. The intermediate concentration solution that leaves condenser 2 returns to regenerator 1. As the pressure in regenerator 2 is almost the same in condenser 2, which is lower than that in regenerator 1, the concentration of the solution can be increased at lower temperature level (95°C) than that required in regenerator 1 to reach the same concentration (150°C).

For the discharging process, the heat released in the absorber is used to produce vapour in the evaporator 2. Since this vapour has a higher temperature (and therefore higher partial pressure), it produces higher end temperatures. In effect, the double-stage process is used to produce the same temperature as in the single-stage, but at lower concentration of solution: $\approx 50 \text{ wt\%}$ (weight percent) in single-stage against $\approx 35 \text{ wt\%}$ in double-stage with NaOH.

The main drawbacks of double-stage processes are the decrease in storage density and the complexity of the system, which needs more tanks and heat exchangers.

EMPA intends to build a double-stage prototype [48]. Calculations for such a double-stage system lead to a storage density of 250 kWh/m^3 .

TCA (Thermo-Chemical Accumulator): It is probably one of the most achieved projects [48] combining absorption and solar technologies with a technical mastery of the different components of the system. The study was directed especially in storage for cooling applications [80] by the SERC (Solar Energy Research Center, Sweden) and their industrial partner ClimateWell AB.

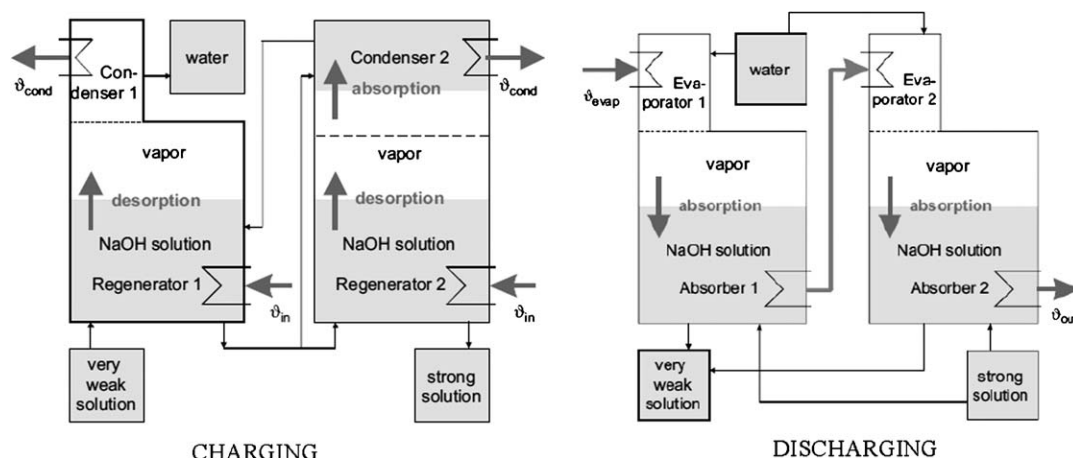


Fig. 11. Operation principle of double-stage closed absorption process [48].

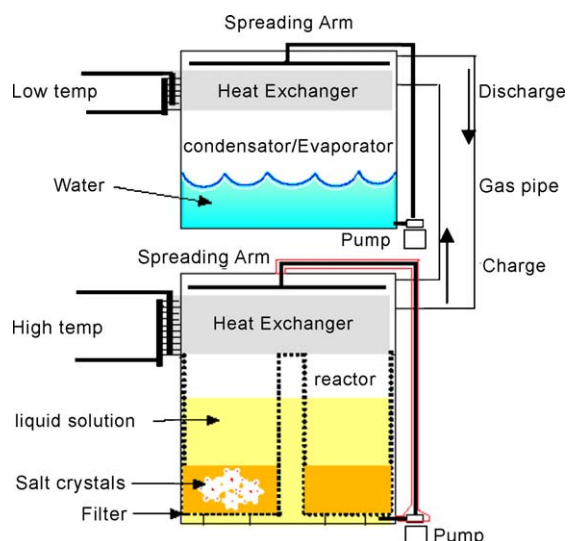


Fig. 12. Schematic of single unit TCA (Source: ClimateWell AB) [80].

However, the system can deliver either cooling (cooling mode) or heating (heating mode). Crystallization, a long time bottleneck point, has been overcome and that enables the enhancement of the storage density and the COP with a so-called “closed three phase absorption” (LiCl solution, salt crystals and water) [80,81]. The process is similar to that of EMPA. The storage density experimentally reached is 253 kWh/m³ of LiCl salt. However, the high price of LiCl (Table 2) led the authors to dismiss prospect of long-term storage, as said before [8,23].

Researches are actually continued for the improvement of heat exchangers and the global design, so that the cost can be decreased [61]. Other salts are also under studies. A machine based on this technology (Fig. 12) is actually commercialised by the society ClimateWell [81]. It can be noticed that the condenser and the evaporator are combined as well as the desorber and the absorber (reactor). For charging, poor solution is pumped over the heat exchanger and comes closer and closer to the saturation point so that solid crystals are formed and collected in the vessel, as they fell under gravity. A sieve prevents them from following the solution into the pump. The water vapour, which is desorbed, flows into the condenser by the gas pipe.

The process is reversed during discharging, where the solution becomes unsaturated on the heat exchanger by absorbing the water vapour produced in the condenser (which becomes the evaporator). The poor solution falls into the vessel where it becomes saturated because of the dissolution of some crystals. The heat of evaporation is provided either by the building (cooling mode) or by the environment (heating mode). The heat of condensation and binding energy release is transferred to the environment (cooling mode) or to the building (heating mode). The main features of the machine are given in Table 3.

PROSIS (PROCédé de Stockage Solaire Inter Saisonnier) [62]: This project, currently coordinated by the LOCIE (Laboratoire Optimisa-

tion de la Conception et Ingénierie de l'Environnement, Chambéry in France), is interested in the development of long-term solar energy storage devices for house heating. The system is based on closed absorption. The project plans to store the rich solution with crystal in order to increase the energy storage density. Static simulations on some potential working pairs have been performed and the consideration of a lot of other parameters, thermodynamic properties in particular, leads to the choice of LiBr/H₂O, well known in absorption refrigeration processes. A prototype will be built to demonstrate the relevance of this concept.

4.3. Remaining concerns and outlooks

Following the research developments presented before, some challenges concerning SSHS still have to be handled:

- Comparison of systems based on storage density should take all the tanks into account when products of desorption have to be stored: this can divided the storage density more than two. The total storage density, which includes all the components (in particular tanks and heat exchangers), is sometimes hardly higher than that of water because of space required by the setting up of these components [66]. However, since water storage is not efficient at long-term energy storage, even low energy storage density systems based on sorption are not long way from being of interest.
- Separate reactors have to be preferred to integrated one.
- Components such as storage tanks, heat exchangers and man-power increase the cost of the system to a great extent [19,61,82]. Improvements in their design can allow cost cuts.
- A sufficient rate of sorption is necessary to obtain a usable delivered power. This can demand materials combination [25,54,68] and a special design of the sorbent bed [54,75] especially for solid sorbents.
- Sorption and thermochemical systems always need a low temperature heat source, which supplies them an amount of energy (for evaporation between 5 and 10 °C or more) almost equivalent to the quantity of useful heat that can be expected from the systems [23,54,70,78]. This source, geothermal for example, has to be available in winter. Furthermore, this source needs to be free, for the system competitiveness [82].
- A risk of water solidification in pipes (circuits) during winter has to be handled for many pairs involving water.
- The number of operation cycles is limited [18] because after many thousand cycles, sorbent has to be changed [19], however this problem is not acute for long-term storage systems.
- In some applications, the critical point remains the discharging temperature [54]. It is necessary to raise the temperature of the sorbent from the ambient temperature (of storage) to the discharging temperature or higher, which results in sensible thermal losses at operations starting and ending.
- SSHS appear to be very complex, especially in closed systems using water as working fluid with difficulties of maintaining long time high vacuum [18,19].
- The current materials studied in closed adsorption do not meet SSHS purposes [66]. They appear to be more suitable for heat

Table 3

Claimed performances of TCA' ClimateWell 10 machine [81].

Mode	Storage capacity ^a	Maximum output capacity ^b	Electrical COP ^c	Thermal efficiency
Cooling	60 kWh	10/20 kW	77	68%
Heating	76 kWh	25 kW	96	160%

^a Total storage capacity (i.e. including two barrels).

^b Cooling capacity per barrel: 10 kW cooling is the maximum capacity. If both barrels are used in parallel (double mode) the maximum cooling output is 20 kW and the heating output is 25 kW.

^c Coefficient of performance (COP) = cooling or heating output divided by electrical input.

pump or cooling applications [50] because of not only the storage density but also the power density of the dense material.

- As said before, material choice is still a critical point: most materials studied are very expensive [54,55,61,66] (Table 2). A lot of experimentations on prototypes, when they are conclusive, lead to heat pumps applications, often because of the materials cost [11,17,55,57].

5. Conclusion

Up to now, studies that have been carried out on SSHS have demonstrated the feasibility of such systems but have ended up in chemical heat pumps or short-term storage machines for those with highest performances. This is mainly due to inapt materials (storage density/efficiency for a given investment and discharging temperature) but also technological difficulties and cost of components. Materials that have been studied are essentially the same that are used for conventional absorption/adsorption machines, i.e. chemical heat pumps and absorption chillers. Studies interested in closed adsorption have led unsatisfying results but those that used closed absorption seem to be promising. Therefore, it would be interesting to continue research in this direction.

Lastly, beyond those different points, common challenges remain as far as sorption systems are concerned, at technological and/or scientific levels: spraying, tightness, design (pressure drop, heat transfer, long time high vacuum maintaining), technological choices (exchanger type), surface treatment/covering of plaques, handling of crystallization, reactor design, falling film flow improvement, heat and mass transfer temperature of collectors, transients management and inertias influence, transients modelling, etc.

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